NEXT GENERATION ANODES FOR LI-ION BATTERIES

FUNDAMENTAL STUDIES OF SI-C MODEL SYSTEMS

ROBERT KOSTECKI

2016 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

Project ID:ES262

Next Generation Anodes for Li-ion Batteries
Fundamental Studies of Si-C Model Systems

- This presentation describes coordinated research task within the five National Laboratory consortium to develop practical Si-based Li-ion negative electrode. (Ref. ES261)
- The primary objective of this effort is to provide basic understanding and effective mitigation of key R&D barriers to implementation of silicon-based anodes.
- The technical approach involves fundamental diagnostic studies of basic properties of the Si anode active and passive components in model systems.

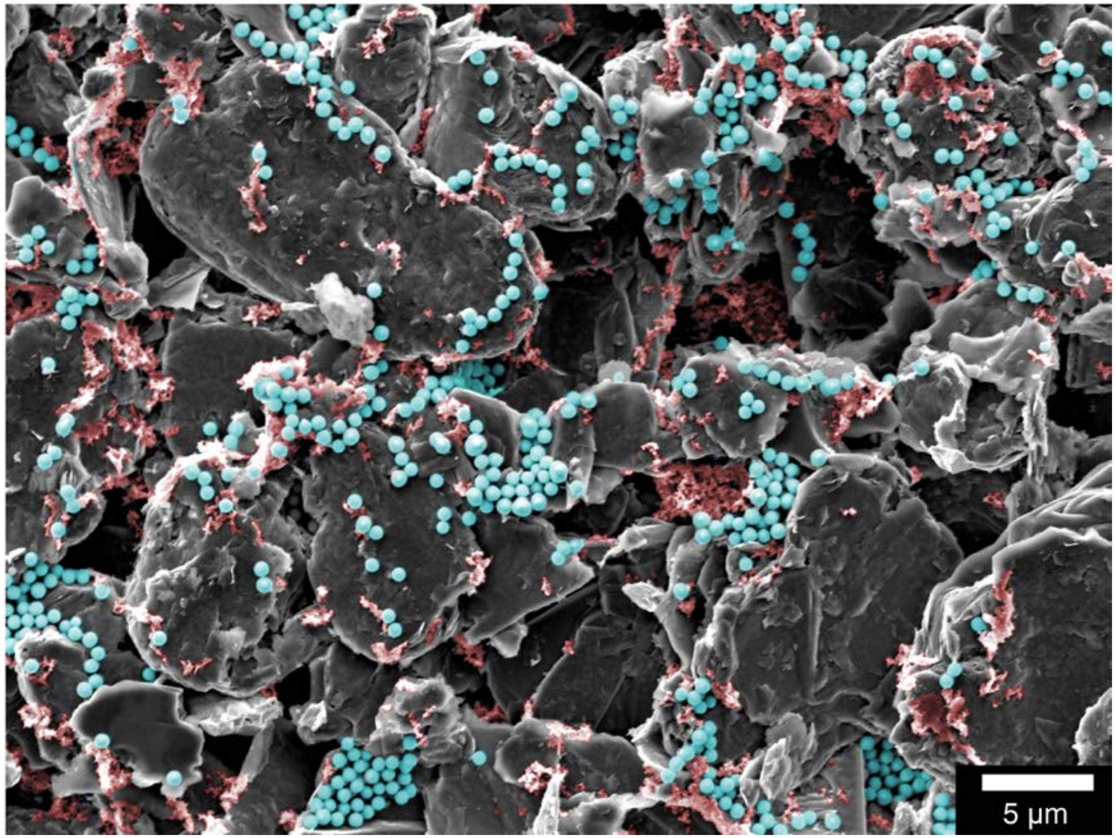
Timeline

- Start: October 1, 2015
  - Kickoff: January, 2016
- End: September 30, 2018

Budget

FY16 Total Funding: $4000K

The Silicon-Carbon Composite Electrode



Jones at al., *Experimental Mechanics, 2014, 54, 971*

- Si/C composite electrode is a complex multicomponent electrochemical systems that incorporate widely dissimilar phases in physical, electrical and ionic contact.
- Basic properties of constituent phases determine the behavior of the composite electrode and the entire Li-ion battery system.

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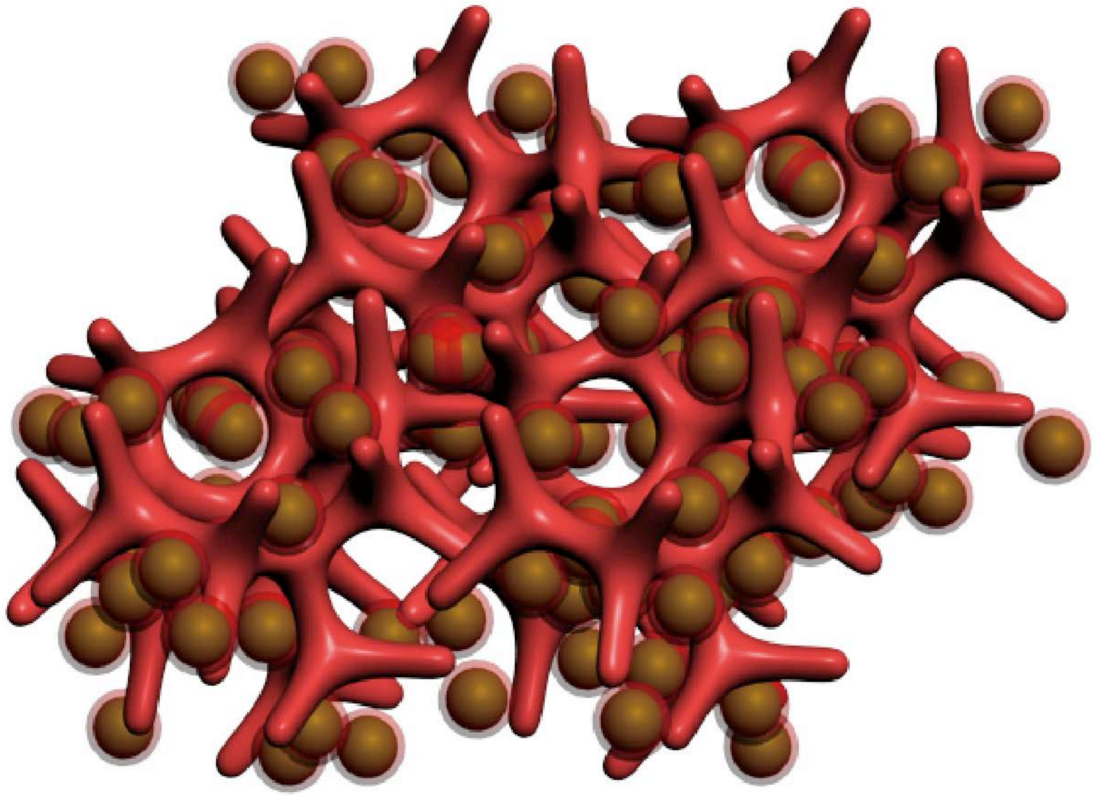

Credit: Yi Cui, Stanford University

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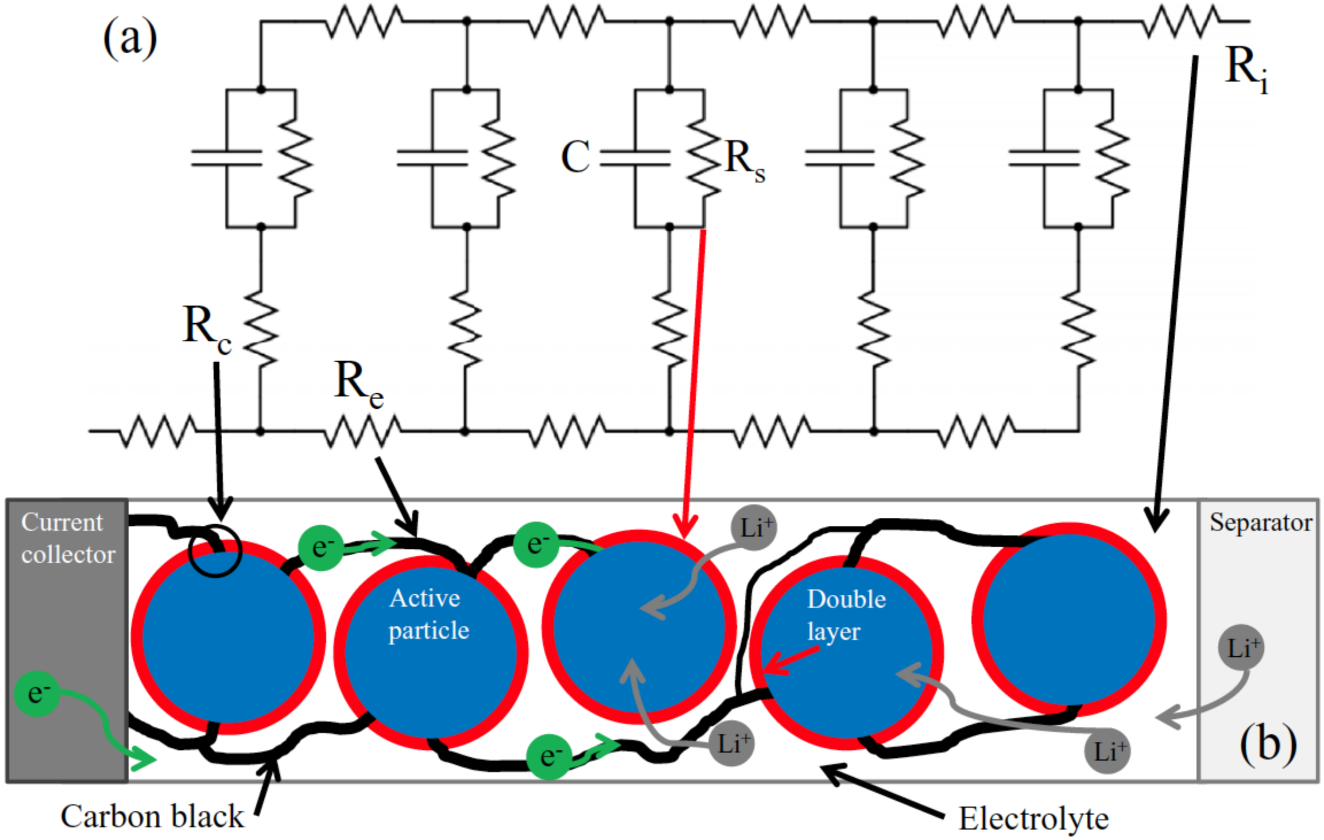


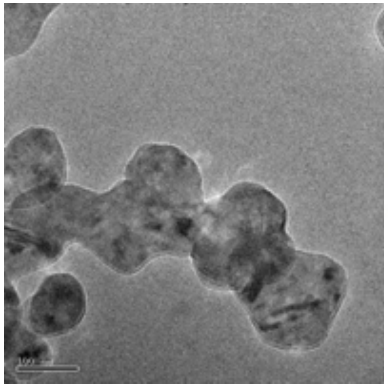
Abarbanel et al., *J. Electrochem. Soc.* 2016,163, A522

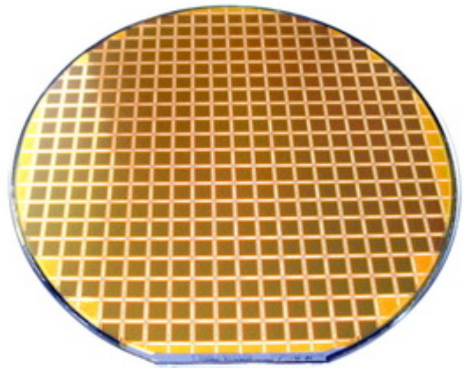
- Si/C composite electrode is a complex multicomponent electrochemical systems that incorporate widely dissimilar phases in physical, electrical and ionic contact.
- Basic properties of constituent phases determine the behavior of the composite electrode and the entire Li-ion battery system.

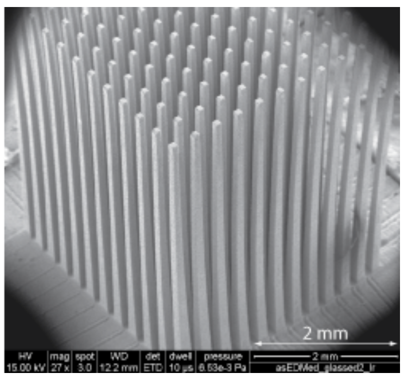
Diagnostic Evaluation of Si-C Anodes
Challenges

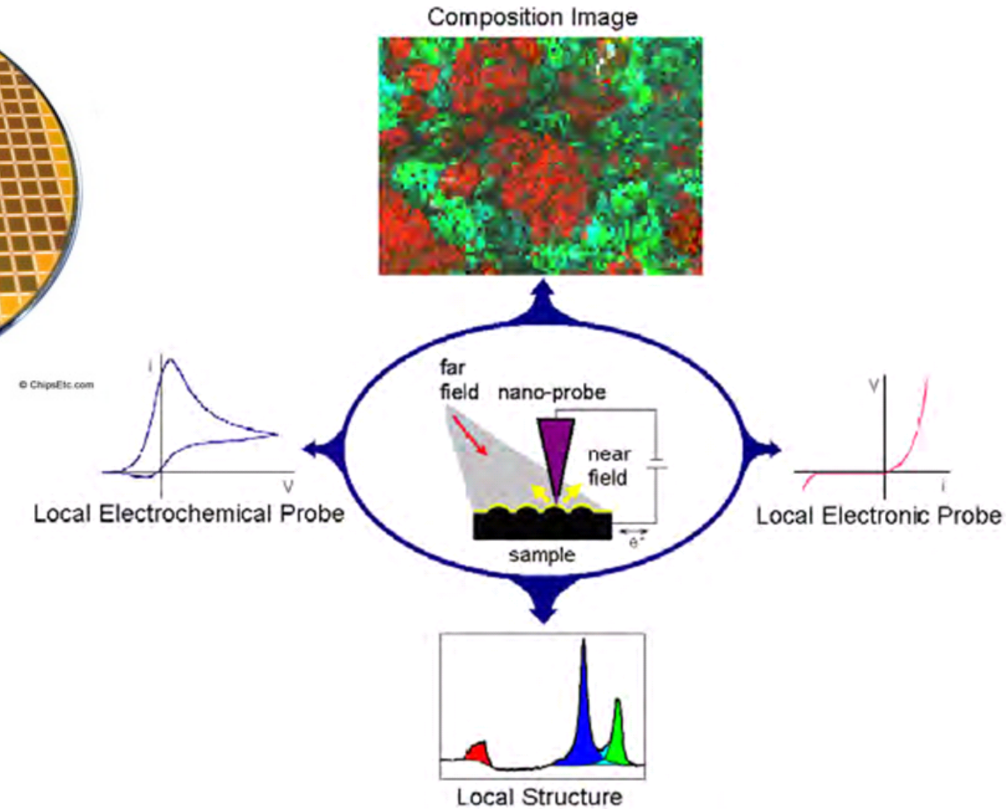
1. Inherent non-passivating behavior of Si in organic electrolytes
   - Large irreversible capacity loss
   - Gradual electrolyte consumption and lithium inventory shift in Si-based cells
2. Large volume changes of Si (320%) during cycling
   - Cracking and decrepitation of Si
   - Loss of electronic connectivity and mechanical integrity

Characterization Strategies for Si/C Anodes





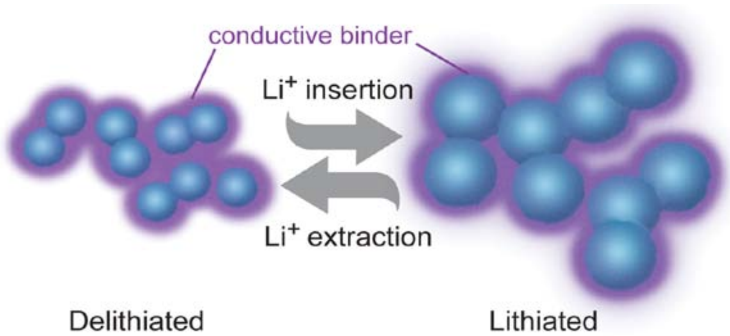




- Design unique experimental methodologies for characterization of model Si, C and Si-C electrodes in a single particle, thin-film and monocrystal configurations.
- Apply *ex situ* and *in situ* optical and X-ray probes capable of sensing surface layers at a submonolayer sensitivity and resolution.

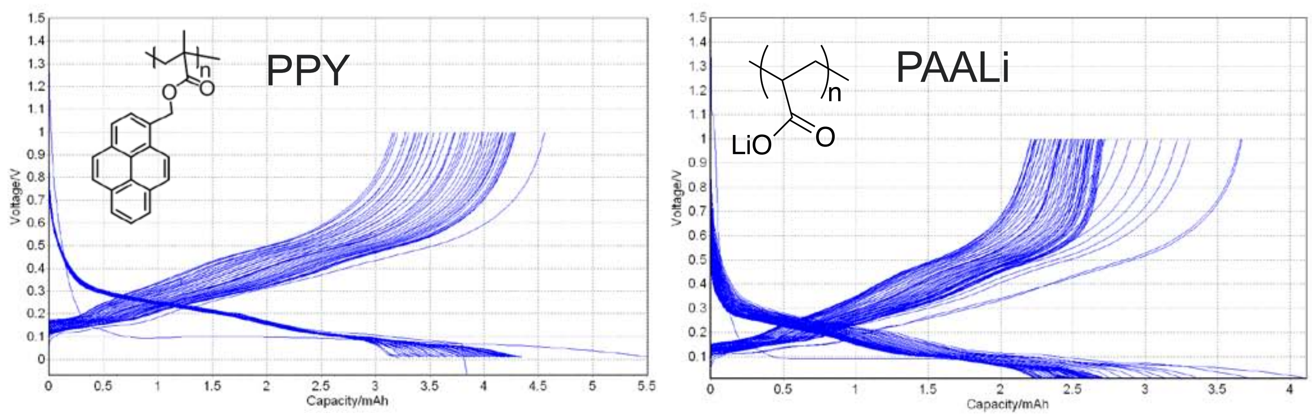
Function and Operation of Multipurpose Binders in Si/C Anodes

Liu et al., *Adv. Mater.* *2011, 23, 4679*



- Electronically and/or ionically conductive
- Chemically stable
- Good mechanical properties
- Compatible with electrode/cell manufacturing processes

15% Si, 73% graphite, 12% binder, 3 mg/cm^2 composite anode



- Electrochemical performance of Si/C electrodes varies strongly with different binders.
- The rate and mechanism of the electrode degradation may depend on the binder properties.

Thorough understanding of the binder modes of operation cannot be gained solely through testing commercial-type devices.

Function and Operation of Binder(s) in Si/C Anodes

Model electrodes preparation and testing

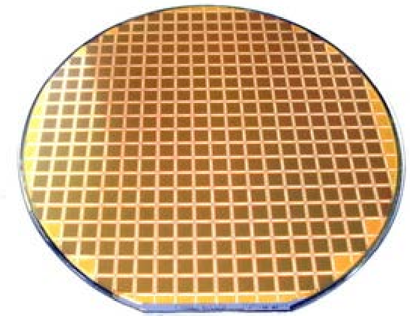
1. Spin-coat PPALi, PVdF, PPy on Cu, p-Si wafer, glassy carbon substrates.

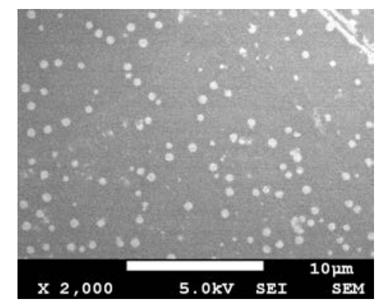
2. Carry out electrochemical measurements of model thin-film electrodes in baseline electrolyte(s).

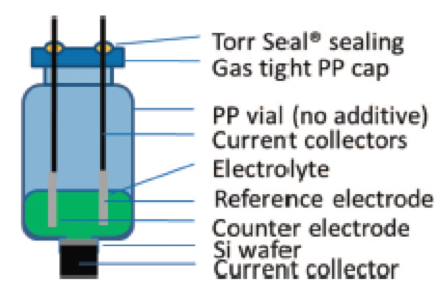
3. Probe *ex situ* binder films after electrochemical tests (CVs, galvanostatic cyling etc)

4. Conduct *ex situ* and *in situ* studies of selected binder thin film electrodes to probe and monitor their phys-chem parameters.

5. Evaluate binders in tested composite Si-C electrodes.



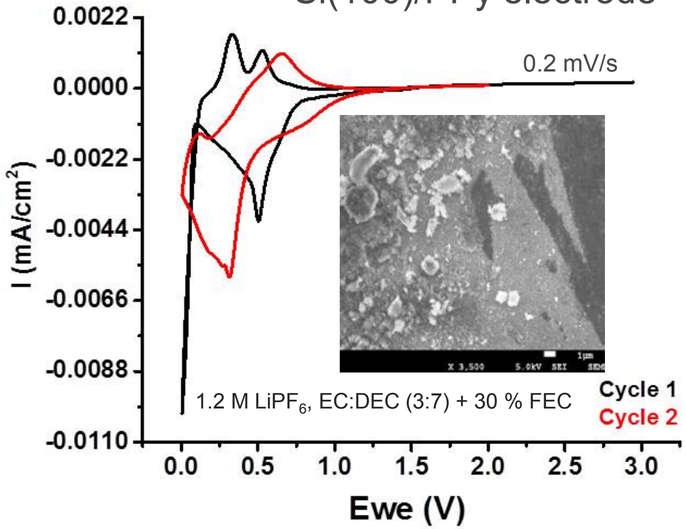


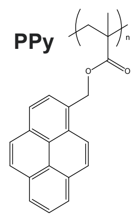


Characterization of Si/Binder Model Electrodes

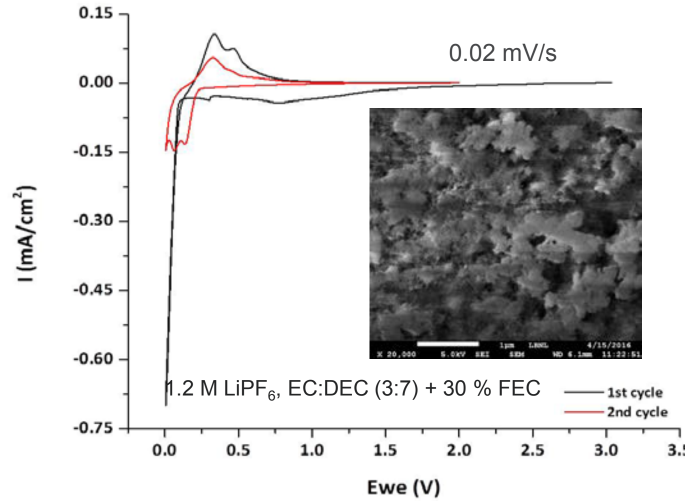
Probing Interfacial Properties of Binders

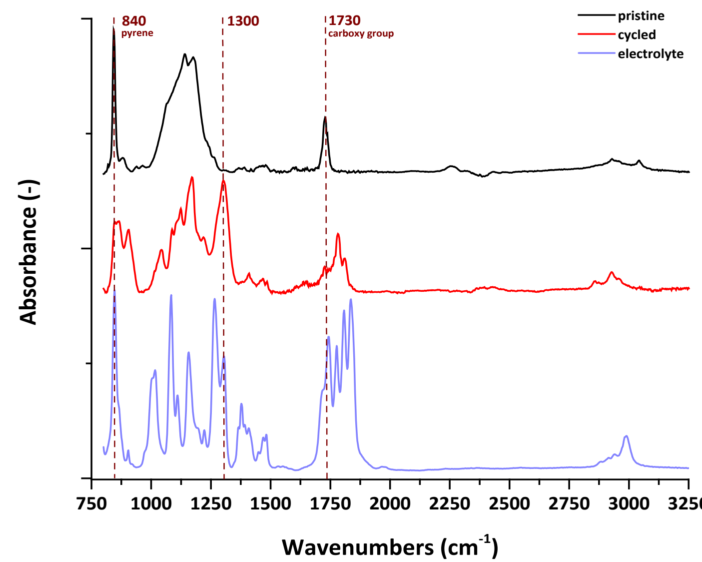
Si(100)/PPy electrode





Si/PPy 2:1 composite electrode

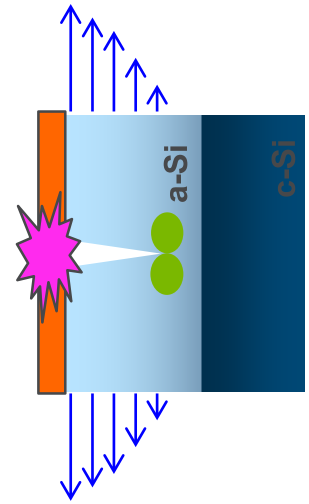




- Preliminary tests show that the model electrodes exhibit more side reactions than the baseline Si/C anodes.
- Electrochemical response varies strongly with different Si-binder arrangements.
- Origins of these interfacial phenomena will be the focus of future studies:
  - Standard electrochemical measurements.
  - Probing ionic and electronic conductivity of binders.
  - Advanced spectroscopy and microscopy of C/binder and Si/binder interfaces and interphases.

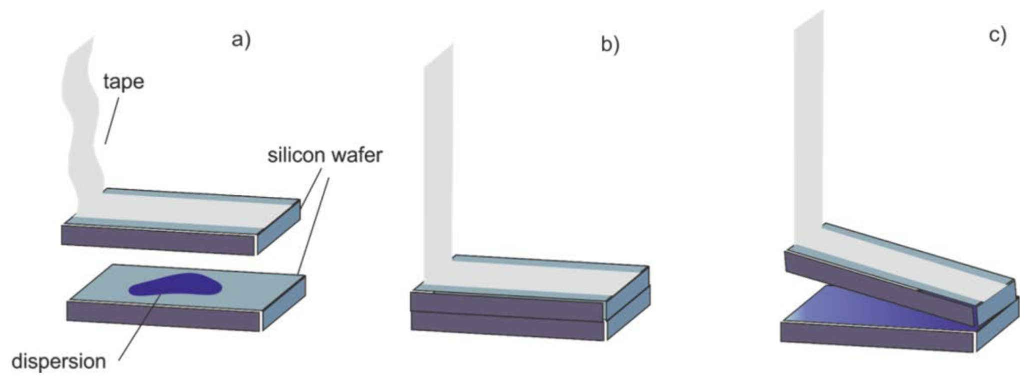
Function and Operation of Binder(s) in Si/C Anodes

Testing mechanical properties of binders before and after electrochemical cycling



- Stress-strain curves for binder thin films.
- Indentation measurements
- Adhesion tests
- Morphology changes.

10 µL dispersion of polymer in NMP between two Si wafer pieces (1 x 1 cm). Adhesion measurements performed at 1 in/min rate.



Vogl et al, Langmuir, 2014,30,10299

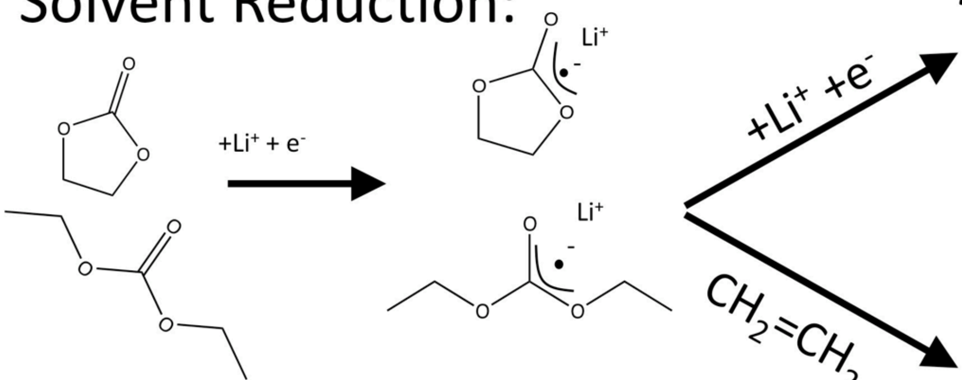
Binder	Dried at 120°C 15 h vacuum [lbf]
PPy	1.47 ± 0.4
PVdF	0.16 ± 0.05

How mechanical properties of the binder help withstand large volumetric changes in Si/C composites and assure composite electrode's mechanical integrity?

Sandia National Laboratories · Oak Ridge National Laboratory · NREL National Renewable Energy Laboratory · Berkeley Lab · Argonne National Laboratory

Solid Electrolyte Interphase at Si/C Anodes

Solvent Reduction:



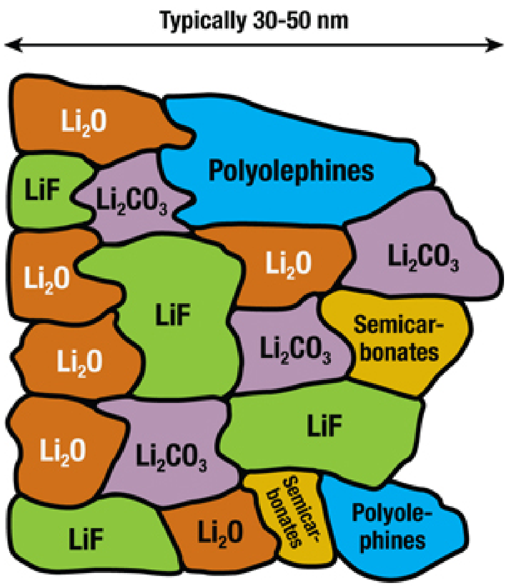
http://webb.cm.utexas.edu/research/research_SEI.html

"good" SEI formation

Li_2CO_3, Li_2O, RCO_2Li, alkoxides
-compact SEI, stable,
ionically conductive

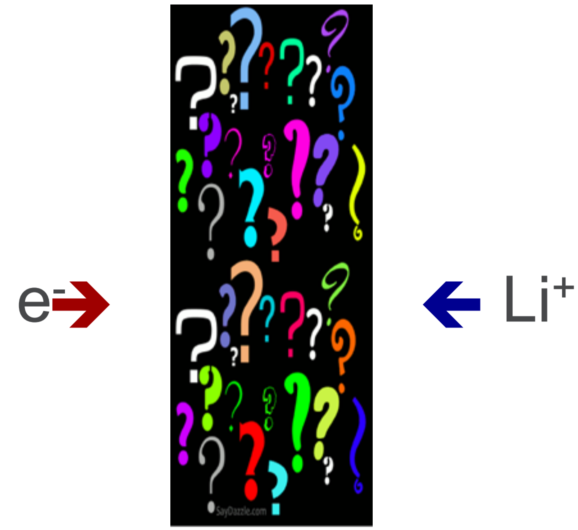
"bad" SEI formation

$(CH2OCOLi)_2$, insulating polymers
-unstable SEI, not ionically
conductive



SEI Interface:
Lithium Intercalation into Graphite

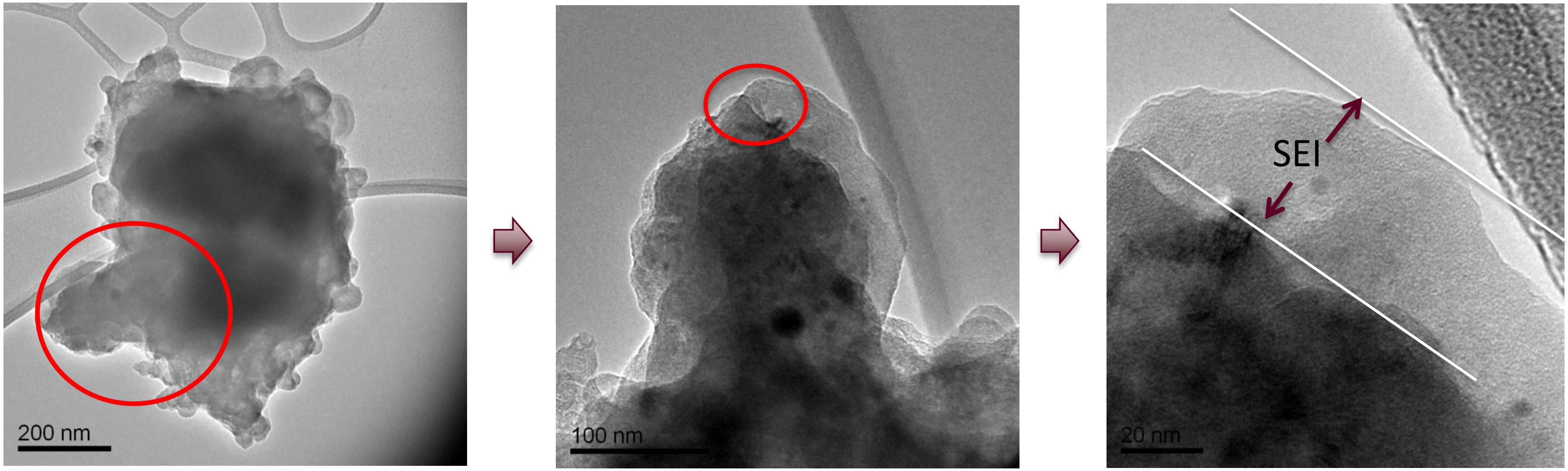
Peled et a;., *J. Electrochem. Soc.*, *144*(8), L208 (1997)



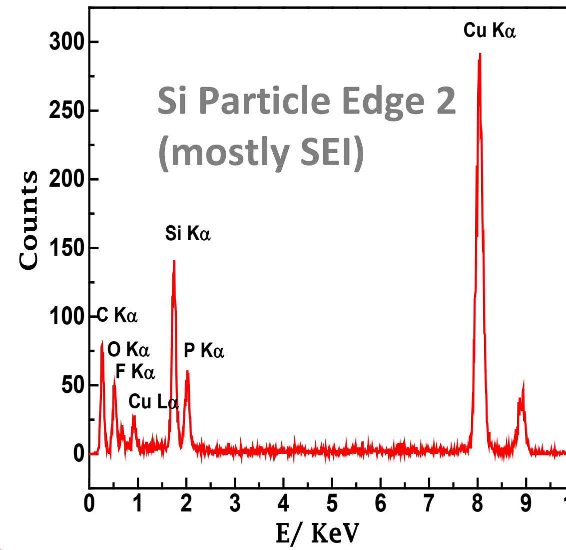
SEI

TEM Analysis of Discharged Si Particles after Formation

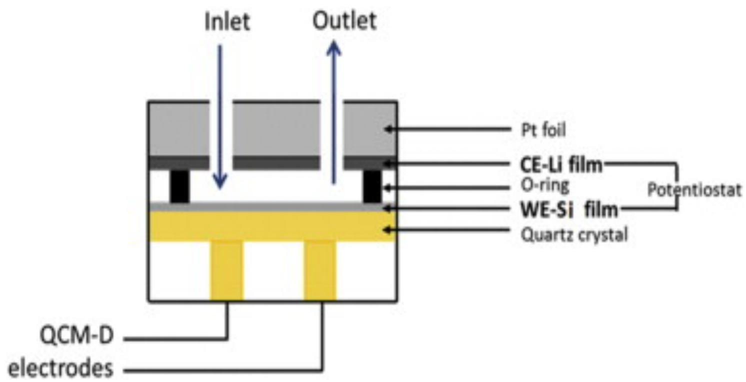
Si Anode in Gen2 +10% FEC Electrolyte

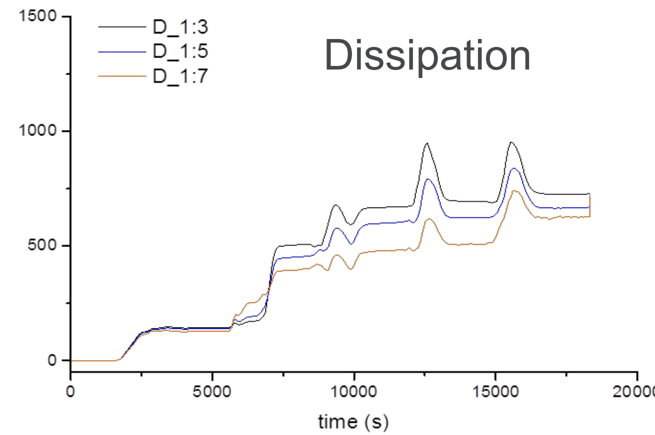


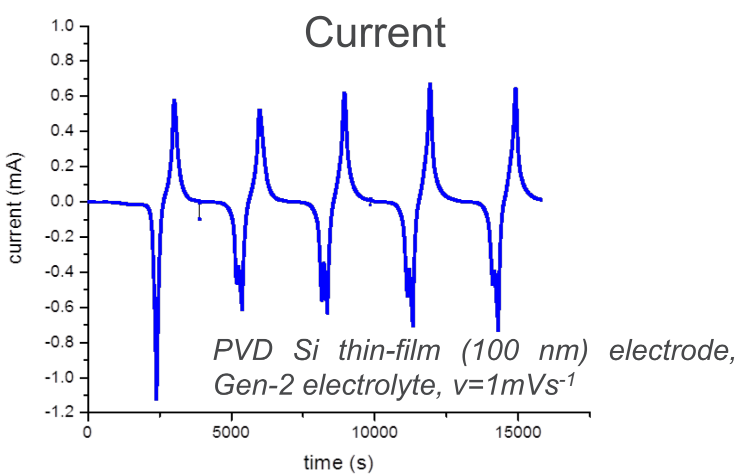
- SEI layer on Si is highly inhomogeneous and it displays poor passivating properties.
- The chemical composition, structure and function of the SEI are not well understood because of:
  - Fine structure and nonhomogeneous properties of electrode/electrolyte interphase.
  - Technical barriers associated with characterization methodologies.

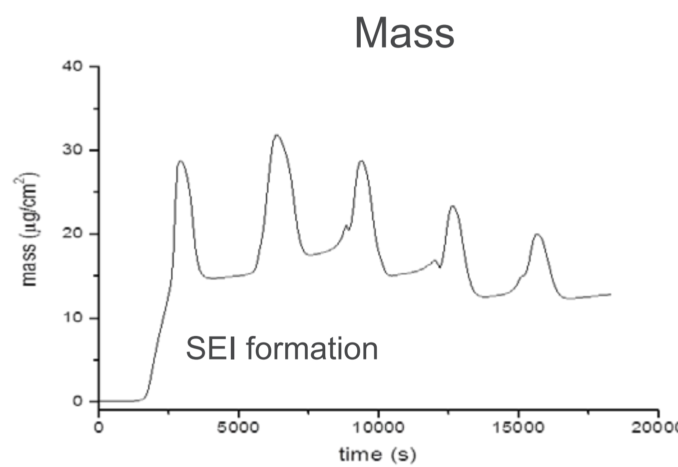


In situ EQCM-D Studies of SEI on Model Si Electrodes



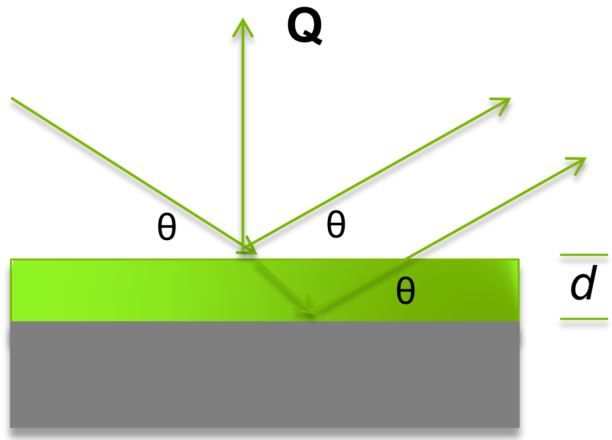


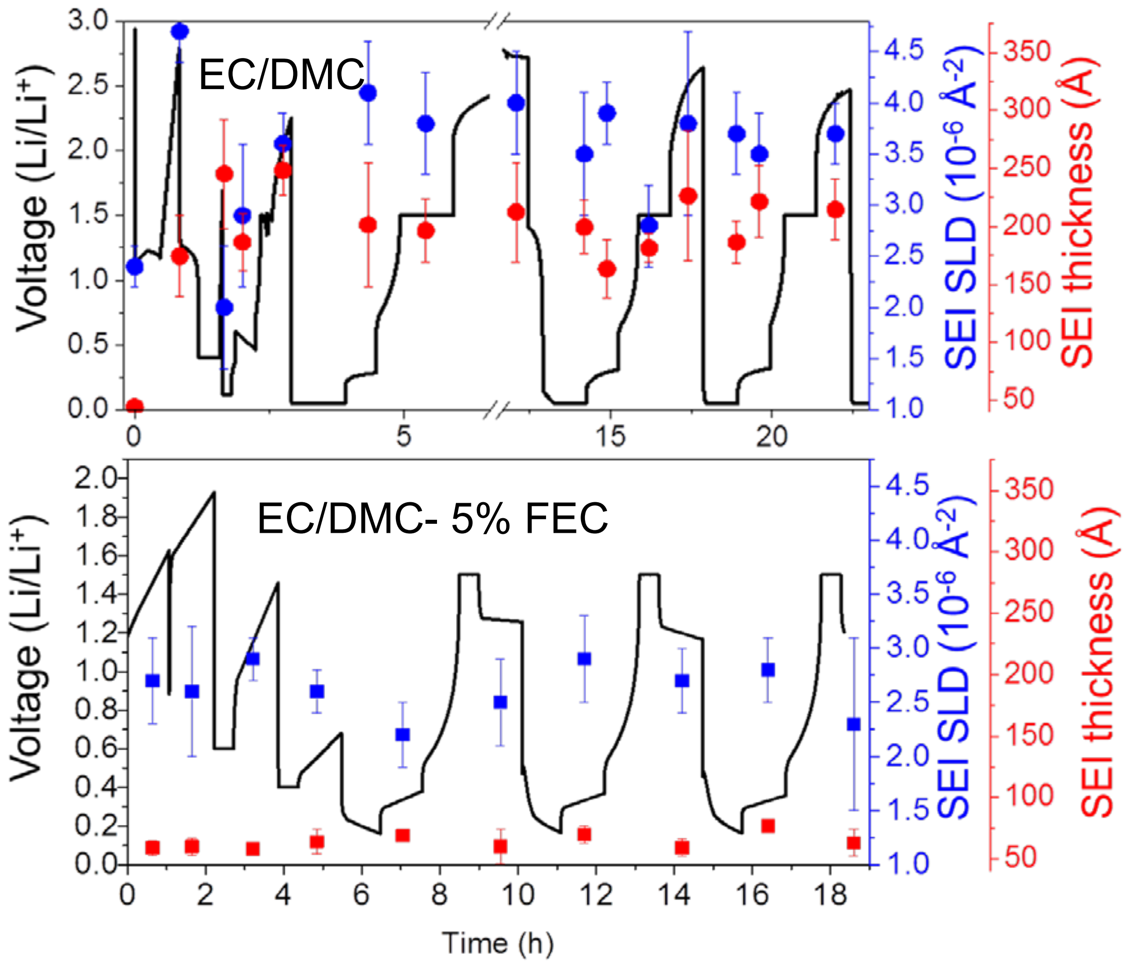




- Goals: (i) evaluate the effect of electrolyte composition, surface composition and morphology on the formation and properties of the SEI, (ii) assess physico-chemical properties of binders.
- Preliminary measurements during initial cycles indicate gradual changes of the mass and mechanical properties of the surface film.

In Situ Neutron Scattering (SANS) Studies of the SEI

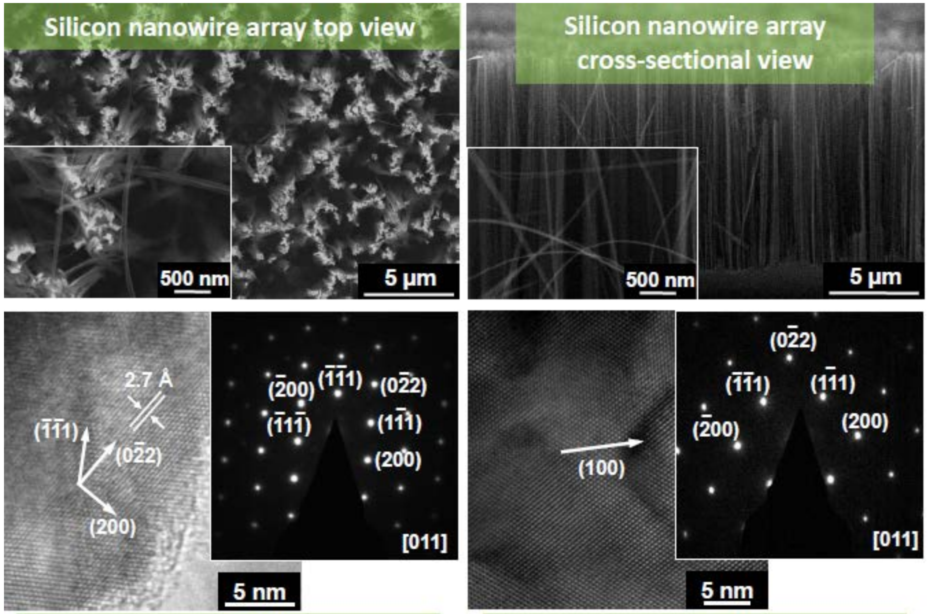




- SEI in presence of FEC electrolyte is ~4x thinner than in base electrolyte. It consists mostly of LiF.
- SEI thickness in base electrolyte varies greatly with cycling.

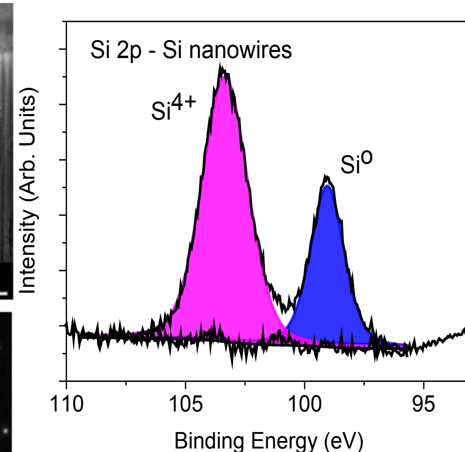
Si Nanowires Model Electrode for Interfacial Studies

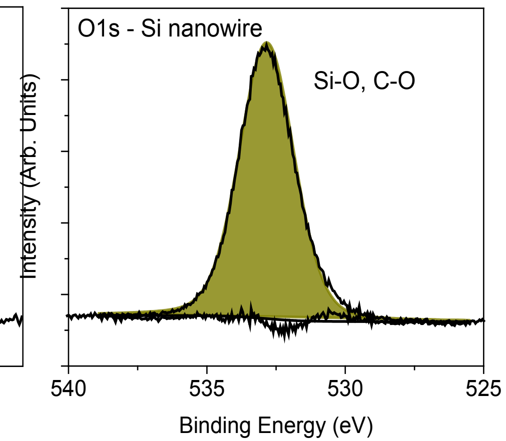
Diameter: 30-60 nm ; Length ~ 10 μm



TEM micrograph indicating [110] growth direction

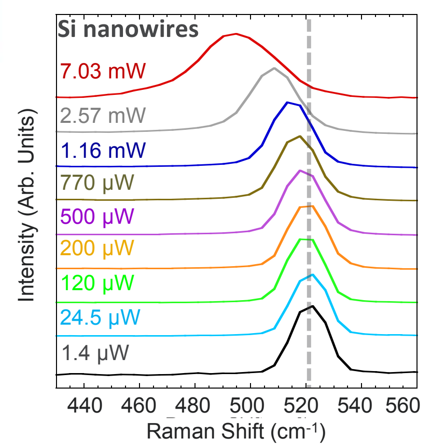
TEM micrograph indicating [100] growth direction

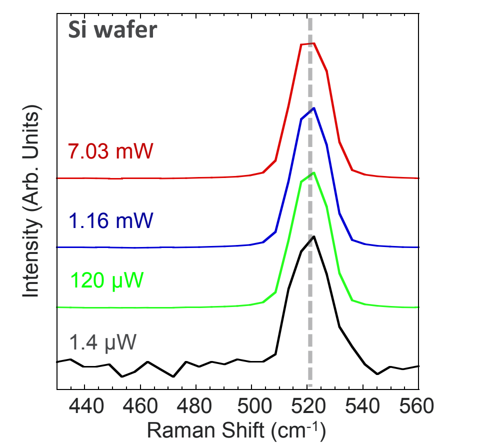




XPS show SiO_x surface layer of thickness < 10 nm that can be removed by a simple etching process

Vaddiraju and coworkers, Materials Letters, 100, 106-110, 2013
Vaddiraju and coworkers, Chemistry of Materials, 26, 2814, 2014
Peng *et al*, Angew. Chem.-Int. Edit., 44, 2737-2742, 2005

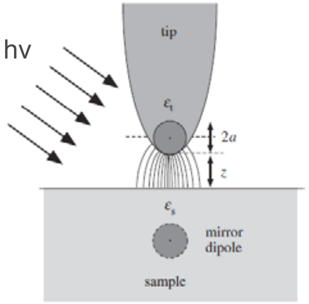




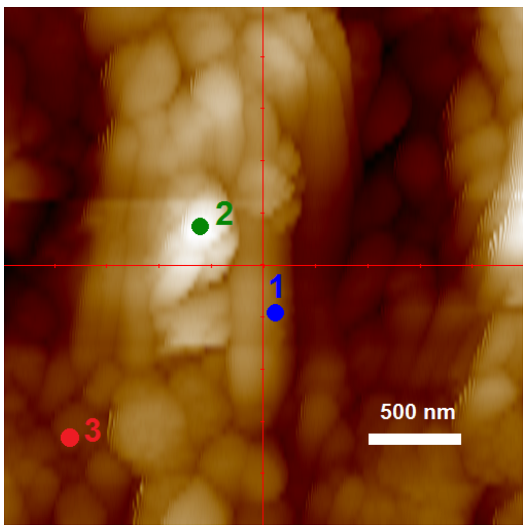
- *In operando* Electrochemical Acoustic Time of Flight (EAToF) on Si-NMC cells (collaboration with Dan Steingart, Princeton University).
- Soft X-ray microscopy and nanotomography of cycled/degraded silicon and silicon-carbon composite electrodes.

Spectral Individuation of the LiBOB-Induced Passivation Film on Si-111 by Near-Field IR Spectroscopy

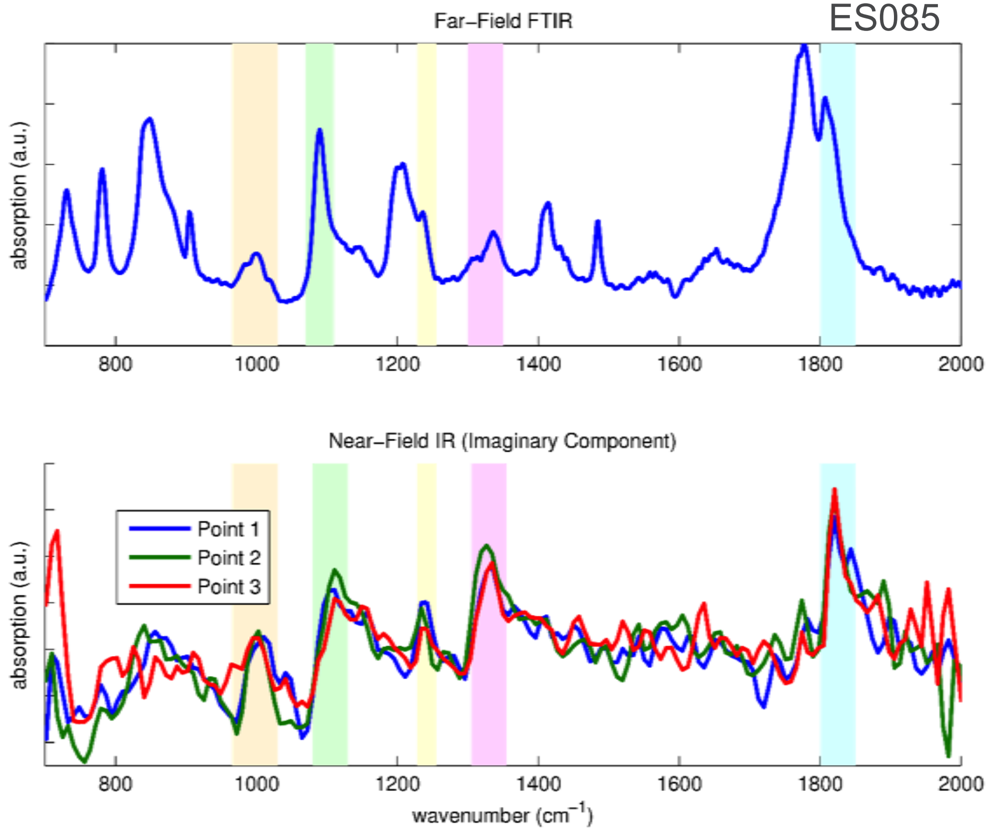
Si(111) wafer at 1.5 V in 1M $LiPF_6$ + 2 % LiBOB, EC:DMC [1:1]



Topography



ES085



- High lateral and axial resolution of the near-field optical probe enable spectral and chemical selectivity to select out peaks associated with a single compound
- Matching early-stage near- and far-field IR spectra allows isolation of the passivating oligomer $LiB_2C_{10}O_{20}$, confirms its presence in the "inner SEI", establishes structure-function relationship

Studies of Solid Electrolyte Interphase at Si/C Anodes

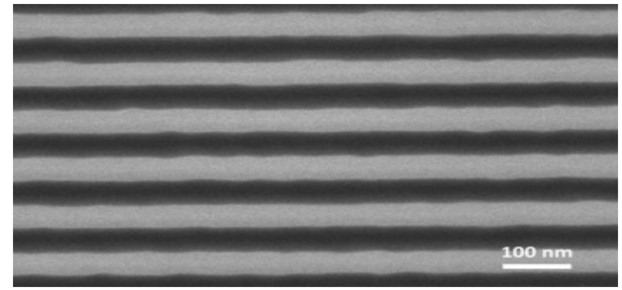
Model Si/C electrodes preparation and testing

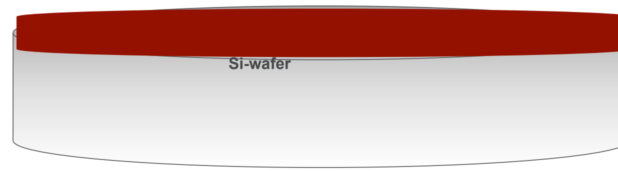
1. Use photo-lithography to produce micro-patterned Si/C electrode.

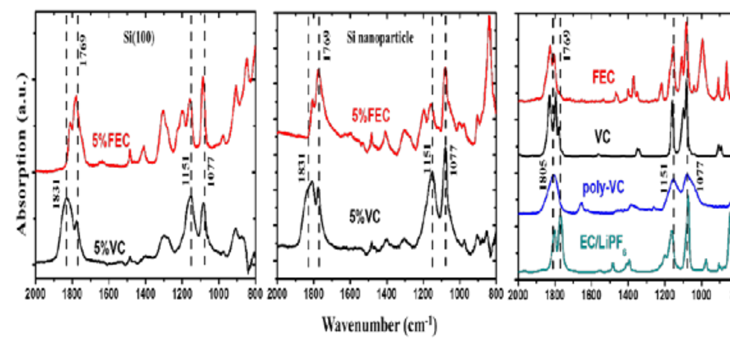
2. Carry out electrochemical tests of model Si/C electrodes in baseline electrolyte(s).

3. Apply *ex situ* and *in situ* optical and X-ray probes capable of sensing surface layers at submicron resolution.

4. Monitor and analyze local SEI formation on silicon, carbon and Si-C boundaries.







Probe interfacial properties and evaluate (in)compatibilty of Si and C surface chemistry on the electrochemical performance of Si/C composite electrodes.

Summary

Initiating Extensive Diagnostic Studies of Model Silicon System

1. Formed collaborative multi-National Lab team to study fundamental phenomena that control the performance of Silicon composite electrodes.
2. Established new and unique experimental capabilities to produce Si, Si/binder, Si/C model electrodes. Initiated integrated electrochemical and analytical diagnostic studies on model systems.
3. Preliminary tests of model Si/PPy electrodes show that the PPy binder is electrochemically stable during initial cycles.
4. More fundamental studies is needed to probe, characterize and evaluate interfacial behavior of model Si/C systems vs. electrochemical performance of the composite silicon anode.

Future Work

- Explore and study range of silicon and silicon-carbon model systems materials to establish correlations between properties of active and passive components and electrochemical performance of Si composite anode.
- Assess failure modes in Si and Si-based materials and electrodes.
- Establish *general rules* of the surface-structure-composition-property relationships for Si-based materials and electrodes.
- Develop new and expand existing *in situ* and *ex situ* diagnostic approaches:
  – Far- and near-field optical micro-spectrometry of electrode/electrolyte interfaces at molecular resolution.
  – Advanced EELS to study lithium transport phenomena in bulk particles, across interfaces, and through grain boundaries.
  – Surface sensitive techniques such as synchrotron XPS, soft XAS, atom probe tomography (APT) and neutron reflectometry to study the composition of interfacial layers as a function of state-of-charge, electrolyte composition, etc.
  – ^{1}H, ^{2}D, ^{6}Li, ^{7}Li, ^{13}C, ^{19}F, ^{31}P Multinuclear Correlation NMR spectroscopy and new *in situ* MAS NMR techniques

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

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